

THE ADDITION OF ALCOHOLS AND
PHENOLS TO FLUOROLEFINS

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EXPLAN

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CHAPTER I

INTRODUCTION

This work describes the base catalyzed addition of organic compounds having a hydroxyl group to fluorocarbonates, or "fluorohydrins", as they are designated for brevity in this discussion. This reaction is interesting from a number of viewpoints; the reaction is not common and offers a number of theoretical considerations, several uses for the products have been proposed and the ethers formed are useful intermediates for the protection of various compounds containing fluorine.

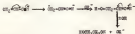
The addition of alcohols or phenols to alkenes in the presence of a basic catalyst is an example of a nucleophilic^a attack on the carbon-carbon double bond, and in such, contrasts to the ordinary additions to alkenes that are catalyzed by acids and therefore initiated by an electrophilic attack of the hydrogen ion or some other electric acceptor. These two types of addition may be illustrated by the following equations of well known additions to the carbon-carbon double bond,

^anucleophilic here is used in the sense that a nucleophilic reagent is one that donates to, or shares its electrons, with an electron deficient reaction center.

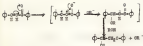
I. Electrophilic attack



II. Nucleophilic attack



It can be seen that in I the initial attack is directed at the electron rich carbon atom and therefore factors that enhance this condition, such as the inductive or polarizing effect of substituents promote this reaction. In II the attack is by the negative ion and it seeks the electron deficient atom as a reaction center, therefore factors decreasing the electron density on a given carbon atom favor the occurrence of a nucleophilic reaction. The reaction shown is the type known as saponification, and is considered a special type of the Michael condensation, wherein a nucleophilic reagent adds to the double bond of an α,β unsaturated ketone, while carbon etc. The space group also is the polarization of the carbon-carbon double bond as does the carbonyl oxygen in a Michael type condensation.



In general, it has been found that esters having two fluorines atoms attached to one carbon undergo nucleophilic addition to the carbon to which the fluorines are attached. It can therefore be assumed that the effect of the fluorine is to decrease the availability of electrons around the carbon to which they are attached to such an extent that this carbon must be relatively positively charged. This final effect might be due to a number of operational causes. The relative electronegativity or the electron withdrawing properties of the halogens, particularly fluorine, is well recognized, as is an effect operating in the opposite direction, that of the tendency for the unshared electrons of the halogen to contribute to partial double bond character of the carbon-halogen bond in resonance structures. This second effect, though postulated to explain the α - β directing influence of halogen attached to a benzene ring, is not necessarily definitively operative in the present case, nor is the concept of polarization of the double bond by the inductive effect of the halogen. It seems reasonable, rather, that the fluorine atoms do decrease the electron density around the carbon to

the unsaturated molecule and that activation or retardation occurs with the approach of the negatively charged addition.

The directive and activating effects operating in addition to the fluorocarbon are certainly not so easily stated as the β activation of the negative ion by the simple electrostatic shift proposed for the Michael reaction. Also, influence of these effects will be complicated by the presence of dissimilar atoms on the carbon other than that bearing the fluorine atoms. Addition of an alcohol to tetrafluoroethene and, of course, give only one final secondary product. Therefore, for the purpose of this investigation, three unsymmetrically substituted fluorocarbonethenes, CF_3CFCl , CF_3CFCl_2 and $\text{CF}_3\text{CF}_2\text{Cl}$ were selected. These alkenes will give structurally isomeric ethers depending on the direction of addition.

Variation in the structure of the addition should also exert an appreciable influence on the course of a reaction of this type. With this in mind, a series of the lower alcohols with increasingly branched structures, methyl, ethyl, isopropyl and tert-butyl, was chosen.

This selection of reactants should give a picture of the directive relationship of fluorine and chlorine and the stability and reactivity of the resulting products should help to clarify the general and sometimes quite unexpected properties fluorine imparts to otherwise common and well-known organic structures.

While not a continuation of this research, some mention

may be made of the possible uses of the compounds prepared. Hulse and Holt have suggested the ethers from addition of the phenols as heat transfer fluids, dielectric media; the more stable types may find uses as lubricants or as additives for lubricants. The alkyl ethers have been used as volatile intermediates for preparation of a wide variety of fluorine compounds, particularly the derivatives of fluorochloromethane acid. Although the medicinal, insecticidal and bactericidal possibilities of these compounds have not been reported, some of their properties, for instance, the enhanced sensitivity of fluorine atoms attached to an ether linkage, would warrant further investigation.

CHAPTER II

PREPARATION OF MONOMERS

The fluorochloroethanes were made by dehalogenation or dehydrohalogenation of the corresponding saturated compound.

Trifluoroethane, $CF_3 \cdot CH_3$ was produced by dehalogenation of 1,1,2-trifluoro-1,2,2-trichloroethane, from KCl_3 , supplied by Kinetic Chemicals Co. The stock was redistilled before use.

1,1-Difluoro-2,2-dichloroethane, $CF_2 \cdot CHCl_2$, was prepared by two methods: 1) dehalogenation with acid of a 1,1-difluoro-1,2,2,2-tetrachloroethane, from KCl_4 , supplied by General Chemical Company and 2) by thermal dehydrochlorination of 1,1-difluoro-1,2,2-trichloroethane, a product of the fluorination of perchloroethane by sulfur trifluoride. Method (2) is described by Mackinnon⁷. Stock prepared by the latter method was washed free of dissolved hydrogen chloride and distilled before use.

1,1-Difluoro-2-chloroethane, $CF_2 \cdot CH_2Cl$, was prepared by dehalogenation with acid of 1,1-difluoro-1,2,2-trichloroethane produced by fluorination of perchloroethane with aqueous trifluoride.

Ethyl, vinyl and iso-propyl alcohols were from regular laboratory supplies and were anhydrous except where indicated in the individual preparations. tert-butyl alcohol was supplied by Columbia Organic Chemicals Company.

Flakes of ginseng grade from General Chemical Company and ginseng grade from Norton Talc Company were both used in the preparations. No objectionable impurities were encountered in the ginseng grade of Norton Talc Company.

Acetone used as a solvent was ginseng grade supplied by Mallinckrodt Chemical Works.

Potassium hydroxide of ginseng grade in pellet form and containing 8% H₂O was used in some preparations where anhydrous conditions were not maintained.

CHAPTER III

METHODS OF ANALYSIS AND IDENTIFICATION

Salogen determinations reported in this work were carried out by decomposing the compound with sodium in benzoyl alcohol according to the method described by Valerfer²⁹ with subsequent titration of chlorine ion by the Volhard method. Fluoride ion was determined as an aliquot portion of the decomposition solution by the best chlorofluoride method described by Miller, Hunt and Rogers³¹ a modification of the method of Koenig³ and of Hoffman and Linstead⁴.

The decomposition method for halogen determination described by Linstead and Dorn³⁰ involving heating of the sample with metallic potassium in a sealed bomb and separation of fluoride ion by a modification of the distillation procedure given by Hutcheson, Vinal and Nelson⁵ was used to some extent during the first period of this work. However, these procedures, though found to be dependable and accurate, are lengthy and the required apparatus was not readily available at all times.

Refractive indices were determined by means of an Abbe¹ refractometer maintained at constant temperature by circulating water through the refractometer from a constant temperature bath. White light was used as a source of illumination.

A Des-Longes type pycnometer modified to include an expansion arm fitted with a ground glass joint was used to determine densities. The pycnometer was carefully calibrated and had a volume of 4.7638 ml. Determinations of the density of a given material were made at the same time as determinations of the refractive index and with use of the same constant temperature bath. This procedure aided in reducing errors in values for molar refractions calculated from the Lorentz-Lorentz formula.

Values of molar refraction from this formula are listed as observed values; calculated values were obtained by addition of the appropriate constants given for the refractivity of the constituent atoms and structural features in Lange¹¹.

Temperatures recorded for the boiling points are uncorrected. Pressures below 10 mm. were measured by a Ralston gauge purchased from the Scientific Supply Company. Pressures of 10 to 150 mm. were measured by a Timmerli gauge; pressures exceeding 150 mm. were measured by a simple open end manometer.

Elemental weight determinations of low boiling compounds were made by the Victor Meyer method.

CHAPTER IV

REVIEW OF THE LITERATURE

Alkyl ethers containing fluorine and of the general type produced by the addition of alcohols to fluorosulfonates were obtained by Meyer^{13,15,16} in 1899 by the action of alcohols on sulfur or metallic carbonates on polyfluorosulfonates. This process was adopted and modified by Deviant¹⁷ recently. In these laboratories a further study was made of the preparation of fluor ethers from esterated compounds.¹⁸

In 1944 Sanford and High¹⁹ reported the preparation of ethers by the addition of alcohols to fluorosulfates in the presence of a basic catalyst. They added ethyl alcohol, n-butyl alcohol, n-pentyl alcohol, n-hexyl, n-octyl, and cyclohexanol, each to one or more of the following sulfates: tetrafluoromethane, trifluoromethanesulfonic acid, and 1,1-difluoro-2,2-dichloroethane. Their reactions were carried out in an autoclave under autogenous pressure and used the alcohols produced by the action of metallic sodium on the corresponding alcohols.

In February of 1948 Miller, Fager and Griswold¹⁵ reported the addition of ethyl alcohol to tetrafluoromethane, trifluoromethanesulfonic acid and 1,1-difluoro-2,2-dichloroethane. They found that these additions proceeded satisfactorily in glass apparatus at autogenous pressure.

A few months later Park, Hall, Lee and Lester¹² reported the reactions of methyl, ethyl, *n*-propyl, *iso*-propyl and *n*-butyl alcohols to trifluoromethanesulfonic acid. They found that anhydrous conditions were necessary for these particular reactions and that potassium hydroxide dissolved in the alcohol being used was satisfactory catalyst and produced ethers in good yield.

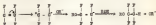
Holmes and Holt¹³ produced a number of arylpolyhaloalkyl ethers of the type previously reported by Harford and Highy by reaction of the arylalkyl naphthalenes with the appropriate saturated polyhaloalkanes. Their method of separation of the ethers involved steam distillation from a strongly alkaline solution and they obtained both the saturated compound and a dehydrohalogenation product, the phenylpolyhaloalkyl ether, from the reaction of 1,2-dichloro-3,4-difluoronaphthalene and sodium phenoxide. They were able to dehydrofluorinate, under more vigorous conditions, the ether $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{Cl}_2\text{F}_2$ obtained from sodium phenoxide and 1,3,2-trichloro-3,4-difluoronaphthalene,

CHAPTER V

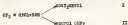
ADDITION OF ALKYLENE AND VINYL TO FLUOROLEFINS

A. Fluorination

These reactions, as has been pointed out in the introduction to this work, are less understood and are thought to be attacked by electrophilic reagents on the fluorolefins. If the fluorolefin is symmetrically substituted, then only one product is possible, regardless of the carbon atom to which the electrophile adds:



If, however, the fluorolefin is unsymmetrical, then formation of either or both of the possible structurally isomeric ethers may take place, depending on the relative induced or permanent positive charge on the two carbon atoms. For example, in the addition of chloride to trifluorovinylidene:



2

Formation of I requires that the carbon bearing the fluorine atom be relatively positive, since the addition is by the negatively charged nucleophilic reagent, while II would require the carbon bearing one fluorine and one chlorine to be relatively positive.

The chlorine shown for this work uses all unsymmetrical and contained the CF_2 group with substitution of combinations of fluorine, chlorine and hydrogen on the other carbon as follows:



Actually, with these chlorines under the conditions studied and with considerable variation in structure of the adding partner, addition was in all cases to the carbon bearing the fluorine atom. This could not have been predicted from the evidence of addition of other compounds to unsymmetrical fluorochlorines. In the addition of primary amines, which presumably form secondary, α , α disubstituted that are subsequently hydrolyzed to β -substituted amides, one or both possible products are formed, depending on reaction conditions.



It was found in the addition of amines, that compound IV

was the only oxide produced at low temperatures, and that both III and IV were acids when the reaction was run at elevated temperatures. Obviously then an increase in temperature is a factor in activation of the possible reaction centers.

Nevertheless, a wide variation in temperature of reaction of alcohols with fluorosulfuric acid (SO_2F_2) in the addition of ethyl alcohol to $\text{CF}_3\text{SO}_2\text{F}$ produced only one ether. Further variations in conditions of the alcohol additions are complicated by the formation of polyalkoxy compounds and also by decomposition of some of the ethers, but even in these cases, no products or fragments were identified that could have come from the direction of addition as shown to produce compound II.

ADDITION OF ALCOHOLS

The first report of the addition of alcohols to fluorosulfuric acid was made in 1941 when Sanford and Wight¹ were issued a patent on additions to $\text{CF}_3\text{SO}_2\text{F}$ and $\text{CF}_3\text{SO}_2\text{OCl}$. Some months after the investigation in this laboratory of the addition of organic molecules to fluorosulfuric acid indicated, Miller, Fager and Griswold² showed that methanol added to $\text{CF}_3\text{SO}_2\text{OCl}$, $\text{CF}_3\text{SO}_2\text{F}$, and $\text{CF}_3\text{SO}_2\text{Cl}_2$ to give ethers of the type $\text{CH}_3\text{OCF}_2\text{SO}_2\text{R}$. After a number of alcohols had been added to several fluorosulfuric acids in this laboratory, Parr,³ at MIT⁴ published a paper on the preparation of the ethers obtained by adding methanol, ethanol, n- and iso-propanol and n-butanol to $\text{CF}_3\text{SO}_2\text{OCl}$.

It was felt that these reports were not of sufficient scope to incorporate with the present investigation, the goal of which was to study the effect of structure of both alcohol and flavonolactone on the rate of addition and the properties of the ethers. Furthermore, it was felt that more work should be taken in the proof of structure of the resulting compounds and in the separation and identification of products other than the saturated ethers. The only products reported by previous investigators were the corresponding saturated bicyclic compounds.

Therefore, the study of the addition of methanol, ethanol, isopropylal and isop-butanol to $\text{C}_6\text{H}_5\text{-CHO}$, $\text{C}_6\text{H}_5\text{-CHOH}$, and $\text{C}_6\text{H}_5\text{-COOH}$ was made. It is known that the substitution of methyl groups for hydrogen atoms in methanol causes an increased concentration of electrons around the oxygen atom thus increasing the basic properties in the order $\text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{C}_3\text{H}_7\text{OH} < \text{C}_4\text{H}_9\text{OH}$. It was thought that this variation in property might affect both the direction of addition as well as the stability of the resulting ether.

The aldehydes were chosen because they are the most easily prepared compounds that would illustrate the effect of various types of groups on one of the carbon atoms. Also it was felt that ethers made from them would be relatively stable. Tetrafluoroethylene was not included since it has a low boiling point (-82°) and would give only a single saturated ether; furthermore, its properties had been investigated rather

completely by the infrared lamp. The ester CF₃COF could have been interesting to study but no satisfactory methods have been developed for its preparation and, in addition, it was thought that toxic compounds might result from its use.

The reaction of each of the alcohols to the esters gave a saturated ether as the principal product with the exception of *tert*-butyl alcohol. The properties of these products are shown in Table I. Various experimental conditions were employed in order to obtain the ethers in as high yields as possible since they vary considerably in stability as discussed below.

General formulas for the saturated and the unsaturated ethers are shown respectively by I and II below.



I



II

In which R represents an alkyl group and T represents fluorine, chlorine or hydrogen. The *tert*-butyl ether may be considered a disproportionation product of an original unsaturated ether, though it seems doubtful that the saturated compound exists for any length of time at the temperature to which it was necessary to raise the reaction in order to obtain reaction.

In a number of cases rather unexpected products were

TABLE I

SPECTRAL PROPERTIES OF MONOMERS AND POLYMERIZATION

Monomer	$\lambda_{\text{max}}, m\mu$	ϵ_{max}^a	ϵ_{max}^b	ϵ_{max}^c	η_{sp}^d
$\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_3$	65.4 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$	50.0-52.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_5$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_4$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_3$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_2$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_1$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_0$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCO}_2\text{C}_6\text{H}_4$	55.0-56.0 (100m.)	1.0000	1.0000	10.0	1.00

^a λ_{max} (m.) 55.0 (100m.) 10.0^b λ_{max} (m.) 55.0 (100m.) 10.0^c λ_{max} (m.) 55.0 (100m.) 10.0^d λ_{max} (m.) 55.0 (100m.) 10.0^e λ_{max} (m.) 55.0 (100m.) 10.0^f λ_{max} (m.) 55.0 (100m.) 10.0^g λ_{max} (m.) 55.0 (100m.) 10.0^h λ_{max} (m.) 55.0 (100m.) 10.0ⁱ λ_{max} (m.) 55.0 (100m.) 10.0^j λ_{max} (m.) 55.0 (100m.) 10.0^k λ_{max} (m.) 55.0 (100m.) 10.0

found. For example, stable, high boiling compounds were formed by continued reaction of ethoxy-1,1-difluoro-2,3-dichloroethane, $\text{EtOCH}_2\text{CHCl}_2$, and ethoxy-1,1,2-trifluoro-2-chloroethane, $\text{EtOCH}_2\text{CHFCl}$ with sodium ethoxide in ethyl alcohol. Halogen analysis and calculation of molar refraction indicated that two additional ethoxy groups had entered the molecule. For the ether from trifluorochloroethane and ethyl alcohol, three polyethoxy structures are possible, depending on the intermediate steps of the reaction:



The product obtained was subjected to hydrolysis by concentrated sulfuric acid and ethyl fluoroborate was separated from the reaction mixture. Only a product of structure VI₂ of the orthoester type, could have produced this result. The hydrolysis is in keeping with the susceptibility of ketal orthoesters to acid hydrolysis and their relative stability in alkaline media.

There is little evidence for decision between the two methods of formation of the orthoesters. The two fluorine atoms on a carbon atom with adjacent ether linkage are known to be reactive. Therefore the Williamson type of reaction seems reasonable, although it is not the usual method of making orthoesters except for the orthoformates from chloroform and sodium alkoxides. Formation through the coordinated loss of hydrogen fluoride and addition of alcohol is equally plausible, though the addition of the third ethoxy group to that end of the molecule requires that the polarizing effect of the attached ethoxy groups be such that the carbon bearing the ether linkage be made relatively positive. These ether linkages have unshared electron pairs on the oxygen atoms, as do the halogen atoms, and are considered electron releasing in resonance structures in benzene substitution reactions although the permanent polarization of the ethoxy groups and halogen atoms is electron withdrawing. Therefore either



could be operative, or any combination of the two effects, so that the final result leaves the carbon with other ligands positively charged.

The esters CF_2COCl_2 and CF_2COCl were considerably more reactive than the more nearly symmetrical CF_3COCl . This could be expected from their markedly unbalanced structures and was shown particularly by their reaction with tert-butyl alcohol. CF_2COCl_2 yielded an addition product at atmospheric pressure and a temperature of 33-45° and CF_2COCl was quite unreactive under similar conditions. When CF_3COCl was refluxed for six hours with either tert-butyl or tert-butylate solution at atmospheric pressure, 7% of the ester was recovered and an addition product isolated.

Formation of carbonates from CF_2COCl_2 and CF_2COCl was possible at atmospheric pressure and at the reflux temperature of the alcohol. This type of compound could be made from CF_3COCl only at elevated temperature (135°); the preparation was carried out in an autoclave. Of course, this reaction is not necessarily a reaction of the chloride linkage, as has been discussed previously. In reactions involving CF_2COCl and CF_2COCl_2 with alcohols, the corresponding esters of chloro- and dichloroacetic acids were frequently encountered, especially when the reaction products were in contact with water

for an extended period. Isomers were never obtained from $\text{C}_7\text{H}_5\text{NOCl}$ under similar conditions.

In connection with the reactivity of the diazot, a number of preparations for which no data are presented in the experimental section may be mentioned.

An attempt was made to carry out the addition of phenol to 1-fluoro-2,3-dichlorobenzene, $\text{C}_6\text{H}_3\text{Cl}_2\text{F}$, by refluxing the diazo with a solution of phenol and potassium phenoxide in acetone for two hours. No addition product was obtained.

A considerable number of preparations were made by the addition of the various alcohols to 1,2-difluoro-2,3-dichlorobenzene, $\text{C}_6\text{H}_3\text{Cl}_2\text{F}_2$, and a product was obtained in each case. However, further investigation revealed that the substituted compound from which the diazo was prepared, $\text{C}_6\text{H}_3\text{Cl}_2\text{F}_2$, contained from 10-15% of the isomer $\text{C}_6\text{H}_4\text{Cl}_2\text{F}_2$. The latter compound would produce $\text{C}_7\text{H}_5\text{Cl}_2$ on dehalogenation. Further examination showed that the physical constants of the products obtained with isopropyl $\text{C}_6\text{H}_3\text{Cl}_2\text{F}_2$ were practically identical with those of the addition products of alcohols and phenols to $\text{C}_7\text{H}_5\text{Cl}_2$ and that the yields were in the range of 70-85%, which is about the percentage of unsymmetrical difluorodichlorobenzenes that could be expected to be present. Hydrolysis of these esters produced alcohols rather than α -fluoro alcohols derivatives. This confirms other reports¹ of the isomericism of the symmetrical alcohol $\text{C}_7\text{H}_5\text{Cl}_2\text{O}$.

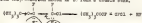
Thermal stability and decomposition of the alkyl ethers

Ethers formed from addition of straight chain alcohols to trifluoromethanesulfonates are relatively stable while those formed from the more reactive 1,1-dichloro-2,2-dichloroethanes and 1,1-dichloro-2-chloroethanes have a tendency to split off hydrogen chloride on long standing.

The stability of fluorosulfates of the type prepared in this research is influenced greatly by substitution of methyl groups for hydrogen atoms on the alpha carbon of the alkyl group. The isopropyl ether from addition to $\text{CF}_3\text{SO}_2\text{Cl}$ was obtained only as a mixture of the saturated and unsaturated compounds, and both isopropyl ethers from addition to $\text{CF}_3\text{SO}_2\text{Cl}$ and to $\text{CF}_3\text{SO}_2\text{Cl}_2$ were unsaturated.

The isopropyl ethers are particularly interesting in that the saturated form is apparently not stable enough under the conditions of this work to be isolated at all. In an early preparation of the addition product of isopropyl alcohol to trifluoromethanesulfonates, an ether was isolated but a variety of decomposition products was obtained; isobutyl chloride, fluorosulfonochloroacetic acid and probably a mixture of ole and trifluoroglass. These products can be accounted for by consideration of the following:

Both the vinyl ether and the butyl fluoride can be accounted for by the following mechanism: the electron-releasing properties of the high-butyl group forced the release of a fluoride ion from the α -carbon in the manner indicated but without rupture of the $\alpha\beta$, C-C bond. The proton was then released from the β -carbon to give HF and the carbocation from the β -carbon moved in to form a double bond,



The HF then formed could easily react with excess high-butyl alcohol to form the corresponding fluoride.

Since decomposition of the isopropyl ethers had been noticed on distillation, a pure sample of $(\text{CH}_3)_2\text{CHOCOC}_2\text{H}_5$ was carefully decomposed as shown in the experimental section by heating at atmospheric pressure. Isopropyl fluoride and dichloroisobutyl fluoride were separated and identified. There was also some indication of the presence of propylene as a fraction boiling in that range was found; it could not be purified with equipment available for the low temperature distillation.

The same mechanism as that proposed for the decomposition of the high-butyl ethers also seems to be applicable in this case.

Reaction of Phenols.

It has been shown previously that alcohols add across the double bonds of unsymmetrical fluorosulfonates to give a single product in which the alcohol group is attached to the carbon atom bearing the greater number of fluorine atoms. However, unless, as noted above, under the proper conditions will add to either end of the carbon to carbon double bond, in each direction, and will therefore give a mixture of products. It was also thought that phenols might add to unsymmetrical fluorosulfonates to give isomeric compounds, since the phenoxide ion is less basic than the alkoxide ion.

Aryl fluorosulfonates have been prepared before. Phenol has been added to tetrafluoroethylene under anhydrous conditions in an autoclave³ and Hefner and Holt¹² prepared various ethers by the reaction of various phenoxide with activated fluorosulfate compounds. In Table II is a comparison of the properties of two of the ethers they prepared from the activated fluorine compounds with those obtained by the addition of phenol to the two starting which results when these activated ethers are dehydrohalogenated. In the case of each pair of preparations it can be seen that there is a good agreement in the boiling point, freezing point and refractive index of the ether formed. It seems likely that the same compounds are produced whether the activated ethers or the corresponding vinylidene compounds are used as the starting materials.

TABLE II

REACTION	$\Delta T_{\text{M.P.}}^{\circ}\text{C.}$	$T_{\text{M.P.}}^{\circ}\text{C.}$	n_D^{20}
$\text{C}_6\text{H}_5\text{ONa} + 2\text{ClCF}_2\text{CHCl}_2 \longrightarrow \text{C}_6\text{H}_5\text{OCF}_2\text{CHCl}_2$	48	+54	1.4784(100)
$\text{C}_6\text{H}_5\text{OH} + \text{CF}_3\text{COCl} \longrightarrow \text{C}_6\text{H}_5\text{OCF}_2\text{CHCl}_2$	72	+54	1.4753(100)
$\text{C}_6\text{H}_5\text{ONa} + 2\text{OCF}_2\text{CH}_2\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{OCF}_2\text{CH}_2\text{Cl}$	56	+51	1.4770(100)
$\text{C}_6\text{H}_5\text{OH} + \text{CF}_3\text{COCl} \longrightarrow \text{C}_6\text{H}_5\text{OCF}_2\text{CH}_2\text{Cl}$	57	+52	1.4754(85)

In the reactions involving the substituted compounds it appears that the chlorine of the $-\text{CF}_2\text{Cl}$ group has been replaced by the phenoxy group in a Williamson type of reaction. This is somewhat unusual and Hulse and Salt make this statement concerning it: "General concepts of the chemistry of the organic siliconfluorides indicate that the chlorine atom on carbon atom bearing an fluorine atom should be replaceable. However, this group apparently resists attack and, in fact, seems to have an orientating effect on the adjacent fluorinated grouping."

Since it is now known that phenoxide will add to a number of fluorosilicates it seems reasonable to assume that the replacement of a fairly weak chlorine atom of the $-\text{CF}_2\text{Cl}$ group did not occur as a simple displacement reaction. It is not necessary to assume such a reaction if one considers that in a basic solution the hydrogen atom alpha to the $-\text{CF}_2\text{Cl}$ group may be removed as a proton followed by the loss of a chloride

less to form hydrogen chloride, such an elimination reaction would result in the formation of an alkene and this formation was observed by these investigators.

In order to indicate more fully the probable reaction mechanism, a study was undertaken of the reaction of phenyl with $\text{CH}_3\text{COOPH}_2$ and CH_3COCH_2 . If the Williamson type reaction occurs with the first compound, then $\text{CH}_3\text{CH}_2\text{OC}_6\text{H}_5$ should result. However, if the reaction proceeds via alkene formation, then the isomeric ether, $\text{CH}_3\text{CH}_2\text{OC}_6\text{H}_5$, should result from both saturated fluorocarbons. Considerable difficulty was encountered in separating and identifying the products. It should be pointed out that certain ethers are less stable than others; for example, in the alkyl ethers, as noted, $\text{C}_4\text{H}_9\text{OC}_2\text{H}_5$ is considerably less stable than $\text{C}_4\text{H}_9\text{OC}_2\text{H}_5$. Apparently the more highly substituted the β -carbon the more stable the α -alkylfluoride.

It is reasonable to assume that an ether such as $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ might decompose to give a variety of products; if such is the case, it would explain the fact that an saturated fluorocarbon was identified.

It is difficult to establish the structure of a phenyl fluorocarbon by the method used with alkyl fluorocarbons as noted before and not enough of the difluoroethyl phenyl ether was separated to establish its structure conclusively. However, data obtained from a series of experiments with ethyl indicates that $\text{CH}_3\text{COOPH}_2$ tends to give $\text{CH}_3\text{CH}_2\text{OC}_6\text{H}_5$ ether

ethyl acetate was formed during the reaction^[1].

While these experiments do not completely prove that alifias are required intermediates with compounds containing the $-CH_2Cl$ group, they at least give this indication.

In connection with the method of formation of the phenyl ethane, it is interesting to note that Miller and Salt obtained the same product when sodium phenoxide was reacted with $CF_3Si(CH_3)_2$ as with $CF_3Si(CH_3)_2Cl$. In other words, the following reactions took place,



This ether is the same obtained in the present work from the addition of phenol to $CF_3Si(CH_3)_2$. The possibility of alifias formation in reaction (a) has been discussed above. In Miller and Salt's report, however, no satisfactory explanation is given for the formation of the same end product by reaction (b). In this case, formation of the alifias by dehydrohalogenation is not possible since the fluorosilane is completely halogenated. There is, however, another possibility of alifias formation that should be given consideration. There are a number of experiments recorded in the literature in which treatment of $u.s.v.$ β -halogenated compounds with alcoholic potassium hydroxide resulted in removal of the two halide atoms but not in the expected manner as the hydrogen halide,

For example, Morrison²⁴ treated the dimeric acid of 3,4'-di-*o*-nitrofluorenes with alcoholic potassium hydroxide and obtained an olefin containing no halogen:



Other examples are given by Perkins²⁵,



and by Albert²⁶



Each of these cases is a removal of halogen from a carbon attached to a strongly electron attracting group. The halogens, particularly the two fluorine atoms, attached to the carbons of the halocarbon used by Meyer and Bolt may exert a similar influence since they are highly electronegative. Therefore an olefin may be formed:



It has been shown in this work that addition of phenol to this olefin will produce the ether reported by Meyer and Bolt.

The effect of the addition temperature on the yield of the ether is quite significant. In experiments with tri-

trifluoromethylphenyls and phenol the best yields were obtained at 45° addition at lower temperatures gave lower yields and at 6° no ether was formed. Maximum yields were obtained with the stannic by carrying out the addition at the reflux temperature of acetone which was used as the solvent.

The addition to CF_3COCl was carried out best at 50° where the corresponding ether was obtained in a 50% yield. In this case higher addition temperatures resulted in the formation of trifluoroacetyl phenyl ether. Separation of the product from the reaction mixture by steam distillation also resulted in dehydrochlorination. Since it was difficult to remove the substituted ethers from the desired products, care had to be exercised to prevent their formation. The ether from CF_3COCl also dehydrochlorinated rather easily. On the other hand the compounds prepared from trifluoromethylphenyls were resistant to alkali. For example, the phenyl ether was refluxed with 20 percent potassium hydroxide at 110° for 24 hours without any appreciable change.

In Table III are listed some of the properties of several ethers produced by the addition of phenols to various esters.

Further study should also be made of the fact that Hulse and Paul's work of structure was based solely on the assumption that a structure with the two fluorine atoms on the carbon bearing the ether linkage would activate the fluorine sufficiently to react with alcoholic potassium hydroxide. Since their compound reacted with the alkali to give a product

containing no fluorine, they concluded that their proposed structure was correct.

A considerably more straight forward proof of structure by hydrolysis of the ether was carried out as illustrated below for the addition product of phenyl trifluoromethanesulfonate.



Several attempts were made to hydrolyze this ether in a process that would establish the structure of the original ether before the procedure described below was worked out. Presumably, from the original ether $C_6H_5SO_2CF_3$, hydrolysis with sulfuric acid by the method of Young and Turrell²² would produce the phenyl ester of fluorosulfoncarboxylic acid. However, this ester is apparently more easily hydrolyzed than the alkyl esters of the halogenated acid and it could not be isolated by the method cited above. Isolation of fluorosulfoncarboxylic acid was not practical, since this material is difficult to handle and could not be distilled easily from the excess concentrated sulfuric acid required for hydrolysis without decomposition.

The method finally adopted for proof of structure of the *para*-*mp*-(polyhalo)ethane involved the formation and isolation

of the ethyl ester of the balsamitic acid without separation of the acid itself from the products of hydrolysis. Since by this procedure, ethyl fluorobalsaminic acid was isolated, the original ester must have had the structure $\text{C}_6\text{H}_3\text{COOC}_2\text{H}_5$, and thus the reaction proceeds with phenols in a manner similar to that with alcohols.

B. EXPERIMENTAL

ADDITION OF ALCOHOLS

In general, reactions of the fluoroborates with the various alcohols were carried out in glass apparatus at atmospheric pressure. In the case of *tert*-butyl alcohol, however, the use of an retortium with the reactants under subatmospheric pressure was necessary. The temperature of the reaction was determined, as in the reactions of fluoroborates with phenols previously described, by the volatility of the alcohol, susceptibility of the product to dehydration and also by the degree of reactivity of the particular alcohol. A brief outline of the procedure for these reactions carried out in glass is given below; specific details will be found under the descriptions of the individual reactions:

The alcohol was placed in a three neck glass flask equipped with stirrer, reflux condenser with Dry Ice cooled trap attached to the upper end and inlet tube or closed addition funnel. Solid potassium hydroxide (85% conc) was added and dissolved. The alcohol was bubbled into the solution with stirring. Distillation of the reaction mixture with water around the solids either to separate and this product was washed with water until free of alkali and reasonably free of alcohol, then dried and fractionated.



a. One hundred sixty three grams (2.5 moles) of potassium hydroxide was dissolved in 470 ml. (approx. 5.0 moles) of ethyl alcohol in a three neck flask equipped with stirrer, reflux condenser cooled with Dry-Ice and inlet tube projecting under the surface of the liquid. Trifluorochloroethane (127 grams) (1.0 mole) was distilled into the stirred mixture over a period of three hours, increased distill being returned by the reflux condenser. Temperature of the reaction rose to 43° . The reaction mixture was allowed to stand for two hours, then heated to a liquid temperature of 75° for 1 hour at this point there was no reflux of alcohol. The crude product was separated by diluting the reaction mixture with water, washed with water and dried over anhydrous calcium chloride. Fractionation through a small column packed with glass helices gave 110 grams of $\text{C}_2\text{H}_5\text{OCF}_2\text{CFCl}$, b.p. $51.3-51.5^\circ$.

Further identification by halogen analysis, etc. of this ether was not made since this compound had been previously reported and the structure determined. A number of preparations of this ether have been made with yields to a maximum of 55% of theoretical. The ether as prepared above was used in the preparation of the trichloro compound described in (b).

b. Sixty five grams (3.45 moles) of $\text{C}_2\text{H}_5\text{OCF}_2\text{CFCl}$, 126 grams (1.7 moles) potassium hydroxide and 126 ml. (approx. 2.5 moles)

ethyl alcohol were placed in the stainless steel retort and heated with stirring for 3 hours at 150° . The retort was cooled to room temperature before opening. Some pressure was evident and considerable gas escaped when the reaction mixture was diluted with water. The organic layer was separated, washed with water and dried over anhydrous calcium chloride. Fractionation gave only one product, 22 grams of 1,1,1-triethyl-2-fluoro-2-chloroethane, b.p. $0-10$ mm. 47.5° , n_D^{25} 1.4439, d_4^{25} 1.8815, η_{41} (calc.) 16.36 (obs.) 16.38, η_{42} (calc.) 48.8 (obs.) 48.8.

The orthoester, 1,1,1-triethyl-2-fluoro-2-chloroethane was subjected to acid hydrolysis to determine its structure by the following procedure: 10 ml. of sulfuric acid (96%) was added slowly to 15 grams (8.35 mols) of the orthoester with intermittent stirring. After 7 ml. of the sulfuric acid was added, there was no additional production of heat. An additional 3 ml. of sulfuric acid was added, the mixture allowed to stand 30 minutes, then poured into cold water and the organic layer separated. This product was washed five times with cold water and dried over anhydrous calcium chloride. Fractionation gave 4 grams of ethyl fluorochloroacetate, $\text{CH}_3\text{CH}_2\text{OOCCH}_2\text{Cl}$, b.p. $129-130^{\circ}$, n_D^{25} 1.3988, indicating that all three ethoxy groups were on one carbon and that the compound was the orthoester of fluorochloroacetic acid.

ADDITION OF TERT-BUTYL ALCOHOL

Sodium isopropylate was prepared by refluxing isopropyl alcohol with sodium metal until the solution was saturated with the alcoholate at approx. 100°C . 200 ml. of this solution were decanted while hot into the distillation flask and before the temperature of the mixture lowered by cooling in a Dry-Ice acetone bath and 10 grams (0.45 mole) of trifluoromethanesulfonic acid. The mixture was heated with shaking for 20 hours at 100°C , then cooled in an ice-salt bath to approximately -10°C and the contents transferred while cold to the pot of the fractionation apparatus. The contents of the mixture were added to lithium. To avoid decomposition, the product was not heated above 35°C . At this temperature and at atmospheric pressure, one product was distilled and identified as isopropyl fluoride, bp. 13.5°C , anal. wt. (calc.) 71 (obs.) 69.

Pressure in the fractionation system containing the residue from the above distillation was lowered gradually in steps of 15 mm. with the pot maintained at 35°C and the liquid reflux condenser cooling liquid at -8°C . The product was distilled until the pressure reached 30 mm. At this point the alcohol distilled and since previous preparations had shown that the ether and alcohol were not separated by distillation, the remaining material was removed from the pot, cooled three

times with acid water and dried in the refrigerator over anhydrous calcium chloride. Fractionation gave 80 grams of 1,1-dimethyl-2-propyl-1,2-difluoro-2-chloroethane, $(CH_3)_2CHCH_2CHCl_2$, b.p. ± 0.5 mm. 18.0° , ± 765 mm. 145° , d_4^{25} 1.3189, d_4^{35} 1.374, f.p. -34° , 501 (calc.) 50.8 (obs.) 50.8, 57 (calc.) 58.27 (obs.) 51.6.

Addition reactions of isopropyl alcohol to $CF_3 \cdot$ & $CF_3O\cdot$ under other conditions are described in some detail below since the reaction products were of interest although the ether described above was not separated as the final product.

a. Fifty eight grams (0.5 mole) of trifluorochloroethane and 540 ml. of isopropyl alcohol placed in the autoclave with shaking for 20 hours at 100° . The reaction mixture was diluted with acid water, the crude product separated, washed and dried and fractionated by atmospheric pressure to give 640 1.6 grams, b.p. $13.5-13.6^\circ$, identified as isopropyl fluoride, a series of intermediate fractions, and 15 grams of trifluoromethane acid, CF_3COOH , b.p. 163.7° , d_4^{25} 1.4093, d_4^{35} 1.518, 501 (calc.) 51.5 (obs.) 51.6. Physical constants reported ¹² for this acid are b.p. 163° , d_4^{25} 1.4093, d_4^{35} 1.509.

b. Fifty eight grams of trifluorochloroethane and 600 ml. of isopropyl alcohol were placed in the autoclave and heated with shaking for 20 hours at 100° . The mixture was added to a Dry-Ice acetone bath, spread and connected directly to the distilling apparatus. A bath surrounding the upper u. saturated with solid isopropyl alcohol.

above was heated to 100° and all material distillable at this temperature removed. Fractionation of this distillate did not separate the components, therefore the mixture was diluted with water, the organic layer separated and dried. This product decomposed on heating and separated into two distinct layers, the upper one colorless.

The residue remaining in the retort after the first distillation was extracted with ethyl ether, the ether removed from the extract by distillation and the residue fractionated under reduced pressure to give 40 grams of $(\text{C}_6\text{H}_5)_3\text{COH} + \text{C}_6\text{H}_5\text{I}$, b.p. $\pm 100^{\circ}$ mm. $\text{H}_2\text{O}-\text{H}_2\text{O}$, n_D^{25} 1.3402, d_4^{25} 1.043, M_D (calc.) 20.8 (obs.) 21.3. This material was probably isopure and it began to decompose rapidly, forming two distinct layers as noted above. Distillation of these decomposition products gave two fractions: Dist 1, b.p. to 140° and Dist 2, b.p. $140-170^{\circ}$, n_D^{25} 1.4070, probably fluorosulfoncarboxylic acid. Dist 1 continued to decompose, separating again into two layers. A portion of the upper layer was removed and distilled to 170° . The distillate had a refractive index of 1.4070 at 43° , a density less than 1.0, observed benzoic, reacted very slowly with sodium and gave only a trace of halogen on sodium fusion. Consideration of the source and these features indicate that this material was a mixture of diacid tri-isobutylenes.

4. Reaction of 0.3 mole of trifluoromethylmethane with 200 ml. of tert-butyl alcohol or with sec-butyl alcohol and .25 mole of sodium in the retort for 20 hours at 150° gave

some of the tetrahydropyranones. Distillation of the reaction mixture with water gave 65 grams of water insoluble material which, on distillation, yielded 27 grams of material, i.e., 34.3-35.5°, d_4^{25} 1.3596, d_4^{25} 1.3693 and a residue of 26 grams of viscous, clear amber colored material that could not be distilled even after the pressure in the system had been lowered to 2 mm.

In these experiments it seems probable that the lower boiling material produced was the cyclic diene reported by Hancock and Cox³ as having the following properties:

Structure:	$\begin{array}{c} \text{CF}_3 - \text{CH} \\ \quad \quad \\ \text{CF}_2 = \text{CH} \end{array}$
i.e.,	34.3°
d_4^{25}	1.3596
d_4^{25}	1.3693

The viscous material is believed to be a higher polymer of the fluorobiolefin or possibly a copolymer of isobutene and trifluorobiolefin. No further identification of these products was attempted.

REACTION OF 1,1-DIFLUORO-2,2-DICHLOROETHYLENE, $\text{CF}_2 = \text{CCl}_2$



204g (5.83 mols) of potassium hydroxide was dissolved in 500 ml. (approx. 5.5 mols) of ethyl alcohol (99%) and 77 grams (0.73 mols) of 1,1-dichloro-2,2-dichloroethane distilled over a period of 3 hours into the potassium ethoxide solution contained in three neck flask equipped with stirrer and reflux condenser cooled by water at about $3-4^{\circ}$. The reaction temperature rose rapidly to 70° , but was lowered to 40° by external cooling and maintained at this temperature. There was no reflux of liquid during the course of the reaction. After addition was complete, the reaction mixture was cooled to room temperature and diluted with water; the lower layer was separated, washed with water and dried over anhydrous potassium carbonate. Fractionation through a 30 inch column packed with Porapak Q gave 37 grams of ethoxy-1,1-dichloro-2,2-dichloroethane, $C_2H_5OCH_2CCl_2$ (88% of theory). Subsequent preparations averaged 45%. B.P. = 180 mm. 43.4° , d_4^{25} 1.3032, d_4^{23} 1.3043, η 0.1 (calc.) 39.7 (obs.) 39.8, and 4.5 grams of 1,1,1-trichloro-2,2-dichloroethane, $Cl_3CH_2CH_2CCl_2$, b.p. = 46 mm. 110.5° , d_4^{25} 1.4384, d_4^{23} 1.4384, 50% (calc.) 30.8 (obs.) 30.8, 100% (calc.) 30.8 (obs.) 30.8.

The ester, $(C_2H_5O)_2CH_2CCl_2$, was prepared in larger quantity by reacting 50 grams (0.88 mols) of the ether, $C_2H_5OCH_2CCl_2$, with 1.3 mols of anhydrous sodium ethoxide in 200 ml. of absolute ethyl alcohol. The mixture was refluxed for 4 hours, cooled and diluted with cold water. A thick emulsion was formed and the product was extracted from this

reaction with ethyl ether. The ether solution was dried over anhydrous calcium chloride, the ether removed by distillation at atmospheric pressure and the crude orthonitrate fractionated at reduced pressure in a small column packed with glass balls and 21.5 grams of whitecap-2,3-dichlorocyclohexane, b.p. 7-10 mm. 104.5-105.0°, was obtained.

Then carried out as described briefly below, this reaction produced some of the ether or orthonitrate described above as a final product but ethyl dichloracetate was obtained in 38% yield based on the ethyl used. 197 grams (3.0 moles) of potassium hydroxide, 515 ml. (6.0 moles) of ethyl alcohol (99%) and 100 grams (0.81 mole) of CF_3COOH were refluxed (liquid temperature 70°) for 6 hours, the mixture diluted with water and the organic layer separated, washed and dried over anhydrous calcium chloride. Fractionation gave 35 grams of ethyl dichloracetate, b.p. 7-10 mm. 58.3-58.8°, n_D^{25} 1.4351, d_4^{25} 1.2699, 121 (calc.) 43.2 (obs.) 43.3, 1000 (calc.) 30.1 (obs.) 31.2.

Reaction of isopropyl alcohol



100 grams (0.81 mole) of sodium was reacted with 400 ml. of isopropyl alcohol, the solution cooled to 20° in a three neck flask equipped with stirrer and has sealed reflux condenser and 155 grams (1.2 mole) of 1,1-dichloro-2,3-dichlorocyclohexane added dropwise. Temperature of the reaction was

maintained at $50-55^{\circ}$ by external heating and stirring continued for three hours. The reaction mixture was poured on to crushed ice, the organic layer separated, washed with cold water, and dried over anhydrous calcium chloride in the refrigerator. When this product was placed in the distillation apparatus and the pot heated to 50° with the head section condensed at -40° there was no reflux. Therefore the pressure was lowered in small steps to a minimum of 7 mm. and the product fractionated at this pressure to give 125 grams of (1-diethyl)ethoxy-1,4-difluoro-5,5-dichloro-2-pentene, (80% of theoretical), b.p. = 7 mm. $28-30.5^{\circ}$, n_D^{25} 1.3877, n_D^{25} 1.3331, d_4^{25} (calc.) 34.73 (obs.) 34.43.

Addition of *tert*-butyl alcohol



Seventy grams (0.32 mole) of 1,4-difluoro-5,5-dichloro-2-pentene and 225 ml. of a solution of sodium *tert*-butoxide in *tert*-butyl alcohol (saturated at 100°) were placed in the stainless steel container and heated with stirring at 100° for 20 hours. The container was then cooled in an ice-salt bath, opened, and the contents poured into a distillation pot surrounded by an ice bath. Distillation of this material to a maximum pot temperature of 45° at atmospheric pressure gave one cut, b.p. $7.5-12.5^{\circ}$, presumably *tert*-butyl fluoride as had been encountered before in the addition of this alcohol

to trifluoroacetic acid.

The residue from the distillation was removed, diluted with cold water and the organic layer separated, washed and dried. Fractionation gave 34.3 grams of (1²,1²-difluoro)ethoxy-2-difluoro-2,2-dichloroethane, $(\text{CH}_3)_2\text{CHOCH}_2\text{COCl}_2$ b.p. = 4.9 mm. n_D^{25} 1.4314, d_4^{25} 1.1466, Mol (calc.) 27.8 (obs.) 27.8.

ADDITION TO 1,1-DIFLUORO-2-CHLOROETHANE

addition of methyl alcohol



Thirty grams (1.5 mole) of potassium hydroxide was dissolved in 500 ml. (5.8 moles) of methyl alcohol contained in a three neck flask equipped with stirrer and reflux condenser; 150 grams (1.5 mole) of 1,1-difluoro-2-chloroethane was added slowly over the stirrer refluxed, (liquid temperature 27°) for 4 hours. The reaction mixture was diluted with cold water the organic layer separated, washed and dried. Fractionation gave 60 grams of ethoxy-1,1-difluoro-2-chloroethane, (87% of theoretical) b.p. = 130 mm. 27.8-30.8°, n_D^{25} 1.3568, d_4^{25} 1.2330, Mol (calc.) 27.8 (obs.) 27.8.

addition of isopropyl alcohol



Fifty six grams (0.85 moles) of potassium hydride was added to 258 ml. (3.2 moles) of isopropyl alcohol and stirred until dissolved. 137 grams (1.59 moles) of 1,1-difluoro-2-chloroethane was added over a period of 2 hours and the temperature of the reaction rose to the boiling point of isopropyl alcohol. The reaction mixture was diluted with cold water, washed, and dried over anhydrous calcium chloride in the refrigerator. Distillation of this material gave a product of b.p. = 121 mm. 53-55°, n_D^{25} 1.3938, d_4^{25} 1.27°. Calculation of the molar refraction and the fact that some isomerization had taken place to produce traces of hydrogen fluoride indicated that this product was a mixture of the saturated ether and a dehydrofluorination product or vinyl ether.

Fifty grams of the product described above was treated with 25 grams of bromine to convert the vinyl ether to a higher boiling compound. Excess bromine was destroyed by sodium bisulfite, the product washed with water and dried. Distillation gave 14 grams of 1-methyl-2-isopropyl-1,1-difluoro-2-chloroethane, b.p. = 121 mm. 53-55°, n_D^{25} 1.3938, d_4^{25} 1.287, 50.1 (calc.) 52.4 (obs.) 52.7.

THERMAL DECOMPOSITION OF ALKOXYPOLYCHLORETHANES.

Thermal decomposition of the alkoxypolychloroethanes had been observed in a number of distillations, particularly those involving alcohols containing only two fluorine atoms, a sample

of the ether resulting from addition of isopropyl chloride to 1,1-difluoro-2,2-dichloroethane, was thermally decomposed under controlled conditions by the following procedure: 40 grams (0.15 mole) of (1-methoxyethoxy)-1,1-difluoro-2,2-dichloroethane, $(CH_3)_2C(OCH_2CH_2O)CF_2Cl_2$, was refluxed in a glass flask under a condenser cooled by water at $3-4^\circ$, vapor passing through the reflux condenser was led through a 150 cm. tube containing a bed of sodium fluoride to absorb hydrogen fluoride and condensed in a trap cooled by a Dry-Ice acetone bath.

Fractionation of the distilled material gave two cuts: 8 grams of b.p. -48.5 to -5.0° , probably a mixture of propane and isopropyl fluoride and 10 grams of isopropyl fluoride, b.p. -8.8 to -7.0° , Mol. Wgt. (calc.) 48.1 (obs.) 41.5.

Distillation of the residue in the flask after the decomposition described above gave 26 grams of dichloromethyl fluoride, $CHCl_2OOF$, b.p. 69.3° , d_4^{25} 1.3846. Reported boiling point and refractive index of this compound are 73.3° , d_D^{17} 1.3762. Dichloroacetaldehyde was made by reaction of the product with aniline and had a m.p. $113-116^\circ$ (rep. 127°).

A small amount of higher boiling material was not distilled. This was presumably, dichloroacetic acid, which gives no consistent boiling point at atmospheric pressure.

B. HYDROLYSIS

ADDITION OF PHENOL

All reactions of the fluoroborates with phenol and the esters were carried out in glass apparatus, specifically, a three neck flask equipped with reflux condenser, stirrer and suitable inlet apparatus for introduction of the ester. Two portions of the reaction are determined by consideration of the volatility of the ester and also by the susceptibility of the product to dehydrohalogenation. In general, the method of preparation found most suitable was as follows: the phenolic compound was dissolved in acetone, solid potassium hydroxide [80% KX] was added to produce the phenoxide and the ester introduced as the mixture was stirred. After completion of the addition of the ester, the reaction mixture was allowed to stand several hours, then diluted with water and the crude product separated. This product was washed with sodium hydroxide solution to convert unreacted phenol to its soluble salt, washed free of alkali, dried and fractionated through a suitable column.

REACTIONS TO 1,1,1-TRIFLUORO-2-ETHOXYETHANEAddition of phenol

One hundred thirty grams (1 mole) of phenol was dissolved in 300 ml. of acetone, 30 grams (0.75 mole) sodium potassium hydroxide added and the mixture stirred until solution was complete. The trichloroethylene, 115 grams (1.5 mole) was distilled into the reaction mixture through an inlet tube reaching under the surface of the liquid over a period of six hours at a liquid temperature of 40° . The gas-flow condenser was cooled by a dry-ice acetone mixture and a trap cooled by dry-ice placed to condense unreacted olefin. After addition of the olefin was complete, the mixture was allowed to stand several hours at room temperature, diluted with water, washed with aqueous sodium hydroxide solution and dried over anhydrous potassium carbonate. About 110 ml. of crude product was obtained. Very little reflux was noted during the reaction and an unreacted olefin was collected in the trap. The product was fractionated through a column packed with glass helices and gave 30 grams of Phenol-1,2,3-trichloroethylene, $C_6H_3Cl_3O$, b.p. $58.8^{\circ} \pm 4$ mm., n_D^{25} 1.4434, n_D^{20} 1.3874, d_4^{25} (calc.) 1.184 (obs.) 1.175, d_4^{20} 1.15.

ANALYSIS OF COMPOUND



Two hundred seventy grams (2.5 moles) of *o*-cresol was dissolved in 300 ml. of acetone and 36 grams (0.8 mole)

solid potassium hydroxide added with stirring and external cooling of the solution. One hundred forty seven grams (1.87 moles) of trifluorochloroacetic acid was distilled into the stirred solution of sodium and sodium acetate, maintaining at a liquid temperature of 15-40°, over a period of four hours. Unreacted acid was trapped and recycled until consumed. The reaction mixture was then diluted with water, the organic layer separated and washed with a solution containing 1.5 moles of sodium hydroxide and the product dried over anhydrous sodium chloride. Yield of crude, dry product was 134 grams, 71% of theoretical. Fractionation of this product through a 30 inch column packed with Sphex medium gave 166 grams of 2-methoxyphenyl-*m*-1,1,1-trifluoro-2-chloroacetate, $\text{C}_6\text{H}_4(\text{OCH}_3)\text{COOCH}_2\text{CCl}_2\text{CF}_3$, b.p. ± 4 mm. 41.6-41.8°, n_D^{25} 1.4503, d_4^{25} 1.3791, 166 (calc.) 15.79 (obs.) 15.7°.

ADDITION OF ACETIC ACID



One hundred seventy grams (1.5 moles) of *m*-cresol were dissolved in 150 ml. of acetone, 36 grams (0.87 mole) of solid potassium hydroxide added and the mixture stirred until the potassium hydroxide had dissolved. 166 grams (1.66 mole) of trifluorochloroacetic acid was evaporated and distilled through the solution, maintaining a liquid temperature of 15-40°. The mixture was allowed to stand overnight, then diluted with

1.5 liters of water and 1.5 moles of sodium hydroxide added. The crude product was separated, washed free of alkali and dried over anhydrous calcium chloride. Yield of the crude, dry product was 144 grams, 77% of theoretical. Fractionation of this material through a 36 inch column packed with Squalan yields gives 148 grams of *p*-methylphenoxyp-4,1,2-trifluoro-*d*-chlorobenzene, $\text{p-CH}_3\text{C}_6\text{H}_4\text{OCF}_2\text{CFCl}$, b.p. $\theta + 3.7$ mm. 65.0-65.7°, n_D^{25} 1.4512, d_4^{25} 1.2778, 50% (calc.) 13.37 (obs.) 13.61.

Addition of *p*-nitrophenol



One hundred sixteen grams of (1.6 moles) *p*-nitrophenol were dissolved in 300 ml. of carbon, 48 grams of potassium hydroxide added and the mixture stirred until all solid was dissolved. One hundred seventy nine grams of trichlorofluoromethane was bubbled through the solution over a period of six hours, maintaining a liquid temperature of 30° by external heating. The crude product was separated by dilution of the reaction mixture with water. No additional potassium hydroxide was added to the wash solution. The product, ^(dry) dried over anhydrous calcium chloride. Fractionation gave 147 grams of 4-nitrophenoxyp-4,1,2-trifluoro-*d*-chlorobenzene, $\text{p-NO}_2\text{C}_6\text{H}_4\text{OCF}_2\text{CFCl}$, b.p. $\theta + 4$ mm. 67.0-70.6°, n_D^{25} 1.4473, d_4^{25} 1.2837, 50% (calc.) 13.73 (obs.) 13.91.

ADDITION TO 1,1-DIFLUORO-2,2-DICHLOROETHANEAddition of Phenol

One hundred and thirty eight grams (2.0 moles) of phenol was dissolved in 350 ml. of acetone, 45 grams of (0.44 moles) pyridine hydrochloride added and the mixture stirred until all solids had dissolved. The solution was then cooled to 12° and 134 grams (1.14 moles) of difluorodichloroethane distilled into the solution while stirring over a period of two hours. Temperature of the reaction mixture was maintained at 12° by external cooling. The mixture was allowed to stand overnight, then diluted with 1.5 liters of cold water containing 1.5 moles of sodium hydroxide in solution. The crude product was separated, washed free of alkali with cold water and dried over anhydrous calcium chloride. Fractionation gave 137 grams (56% of theoretical) of Phenoxyl-1,1-difluoro-2,2-dichloroethane, $C_6H_5OC_6H_5CHCl_2$, b.p. ± 4 mm. 71.0-71.5°, n_D^{25} 1.4763, d_4^{25} 1.3781, 70% (calc.) 71.2 (obs.) 71.3.

ADDITION TO 1,1-DIFLUORO-2,2-DICHLOROETHANEAddition of Phenol

Two hundred thirty five grams of (2.5 moles) of phenol

was dissolved in 400 ml. of acetone, 200 grams (1.5 moles) of potassium hydroxide added and the mixture stirred until all solid had dissolved. The solution was cooled to room temperature and 115 grams (1.15 moles) of difluoroacetylene distilled into the mixture. Estimated ethine was trapped and recycled, three passes being required for complete absorption of the ethine. Approximately three hours was required for absorption of the ethine and the temperature rose to a maximum of 45° . The reaction mixture was stirred an additional three hours, allowed to stand overnight, then diluted with ether and the crude product separated. This product was washed with sodium hydroxide solution, with water and dried over anhydrous calcium chloride. Fractionation through a packed column at 4 mm. gives

Run	Boiling Point	Yield	d_4^{25}
1	36.0-36.4	40g.	1.4770
2	36.4-37.1	50g.	
3	36.6-37.6	70g.	1.4730

run 3 is $C_2H_2ClF_2$, b.p. at 4 mm. $36.6-37.6^{\circ}$, d_4^{25} 1.4730, d_4^{25} 1.4670, n_D^{25} (calc.) 1.543 (obs.) 1.535. This product was prepared by Cohen and Holt. The above constants are in reasonable agreement with their values. Runs 1 and 2 are mixtures of the estimated ethine described above and the dehydrochlorinated product $C_2H_2ClF_2$. 40 grams of run 1 was refluxed with aqueous potassium hydroxide solution for 4 hours, separated, washed and dried. Fractionation at re-

distd pressure gave a product with refractive index of 1.4934 at 25° and containing 17.7% chlorine. Reported values for the phenyl-vinyl ether is n_D^{20} 1.5045 and the theoretical value for percentage chlorine is 20.3%. Therefore the product obtained by the alkali treatment is probably also a mixture of the saturated and unsaturated ethers, but containing more of the unsaturated than the saturated ether.

PREPARATION OF 1,2-DIFLUORO-3,4-DICHLOROBUTADIENE

1,2-Difluoro-3,4-dichlorobutane



Addition of phenol to 1,2-difluoro-3,4-dichlorobutane at a higher temperature and with separation of the product by a procedure different from that described above for the saturated ether resulted in a dehydrochlorinated product.

The hundred eighty two grams (3.6 moles) of phenol was dissolved in 500 ml. of acetone, 42 grams (0.44 mole) of potassium hydroxide was added and the solution stirred until all solids dissolved. 1,2-Difluoro-3,4-dichlorobutane (800 grams-4.3 moles) was distilled slowly into the stirred mixture over a period of three hours. A heated temperature plate was used during the addition of the olefin. After addition of the olefin was complete, acetone was distilled from the mixture to a distillate temperature of 75°, the residue cooled

and sufficient potassium hydroxide added to convert the phenol to the potassium salt. The mixture was then steam distilled, separated, washed with water and dried. Fractionation through a 10 inch column packed with glass helices gave 193 grams of phenyl-1-fluoro-2,2-dichloroethane, $C_6H_5OCH_2CHCl_2$, (66% of theoretical) b.p. ± 4 mm. $76.0-77.5^\circ$, n_D^{25} 1.3938, d_4^{25} 1.1744, refr. index. 34.76 (calc.) 34.77.

Phenyl-1,1-dichloroethane



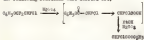
The saturated ether $C_6H_5OCH_2CHCl_2$ readily disproportionates under the previously given conditions of preparation or the conditions of steam distillation in the presence of alkali.

Twenty three grams of $C_6H_5OCH_2CHCl_2$ was refluxed with 50 grams of potassium hydroxide in 100 ml. of water for 24 hours. After the product was separated, washed free of alkali, dried and fractionated, the refractive index was not appreciably different from that of the saturated compound.

Another portion of the saturated ether $C_6H_5OCH_2CHCl_2$ was refluxed with excess powdered potassium hydroxide until all evidence of reaction had ceased, then distilled from the solid. The product was $C_6H_5CHCl_2$, b.p. 146° , n_D^{25} 1.397, ref. index. 18.4 (calc.) 18.4, d_4^{25} 1.4337.

Phenyl-1,1-dichloroethane

To establish the structure of the arylpropylchloroacetates, the following reactions were carried out.



One hundred five grams (0.5 mole) of $C_6H_5OCF_2CH_2Cl$ was mixed with 100 grams (1.5mole) of acetic acid [96] in a three neck glass flask equipped with stirrer and reflux condenser. The mixture was heated with stirring on a steam bath for 45 minutes, cooled to room temperature, 30 ml. of ethyl alcohol (reagent) added and refluxed for 15 minutes. The reaction mixture was then poured into a beaker of crushed ice, the lower layer separated and washed with acid sodium hydroxide solution, with water until alkali free, and dried over calcium chloride anhydride. Fractionation gave 11 grams of $C_6H_5OCH_2CO_2C_2H_5$, b.p. $130-131^\circ$, n_D^{20} 1.3951, n_D^{25} 1.383. These data are in agreement with those published for ethyl phenylacetate and confirm the assumption that the structure of the original ether involves a phenoxy group attached to the carbon bearing two fluorine atoms.

Summary

- I. A number of alkylpolyethylaluminum and alkylarythanes have been prepared by addition of alcohols to fluoroborane.
- II. A number of arylpolyethylaluminums have been prepared by the addition of phenol and cresols to fluoroborane. Two of these were dehydrofluorinated to produce the corresponding unsaturated ethers.
- III. Alkylpolyethylaluminums of the types $\text{ROR}_2\text{PCH}_2\text{CH}_3$ and $\text{ROR}_2\text{PCH}_2\text{CH}_2\text{CH}_3$ have been shown to react further with alcohol in the presence of aluminum ion, to give polyalkylary compounds of the catenar type.
- IV. Thermal decomposition of the ethers formed from highly branched alcohols has been studied and the fragments identified.
- V. A mechanism has been proposed for the thermal decomposition of ethers formed by addition of secondary and tertiary alcohols to fluoroborane.

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Henry G. Brown, III, was born at Fortuna, Florida on March 7, 1918.

He attended Johns University from September 1937, to August, 1941 and was awarded the B.S. degree in 1941, the M.A. degree in 1943 from that institution.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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